Atmospheric Formation and Decay of Air Toxics – Implications for Exposure Assessments

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Air Toxics Exposure Assessment Workshop

Outline

- What chemical processes affect air toxics concentrations in the atmosphere?
  - Destruction through chemical reaction
  - Formation in the atmosphere
- Why do I care?
  - Implications for monitoring network design
  - Implications for modeling studies
  - Implications for other Program areas
- What further research do we need to do?

Quantifying Pollutant Decay

- "Half life": The time for a pollutant to be reduced to ½ of its original concentration

  $t_{1/2} = (1/t^1_{1/2} + 1/t^2_{1/2} + 1/t^3_{1/2} + \ldots\ldots.)^{-1}$ for all processes

  $t_{1/2} = \ln(2)/k_B[B]$ for a second order reaction

- "Lifetime": the time for a pollutant to be reduced to 1/e of its original concentration

  $?_{1/2}=1.0/k_B[B]$ for a second order reaction

Chemical decay processes in the atmosphere

- Reaction with OH radical
  - Important for almost every pollutant
  - usually the most important reaction during daylight
  - OH radicals are recycled
  - Many reactions are temperature dependant
  - Reaction rate depends on the OH concentration which is variable (0.0-9.0e6 in summer, 0.0-5.0e5 in winter)
  - We don’t have good routine measurements of OH

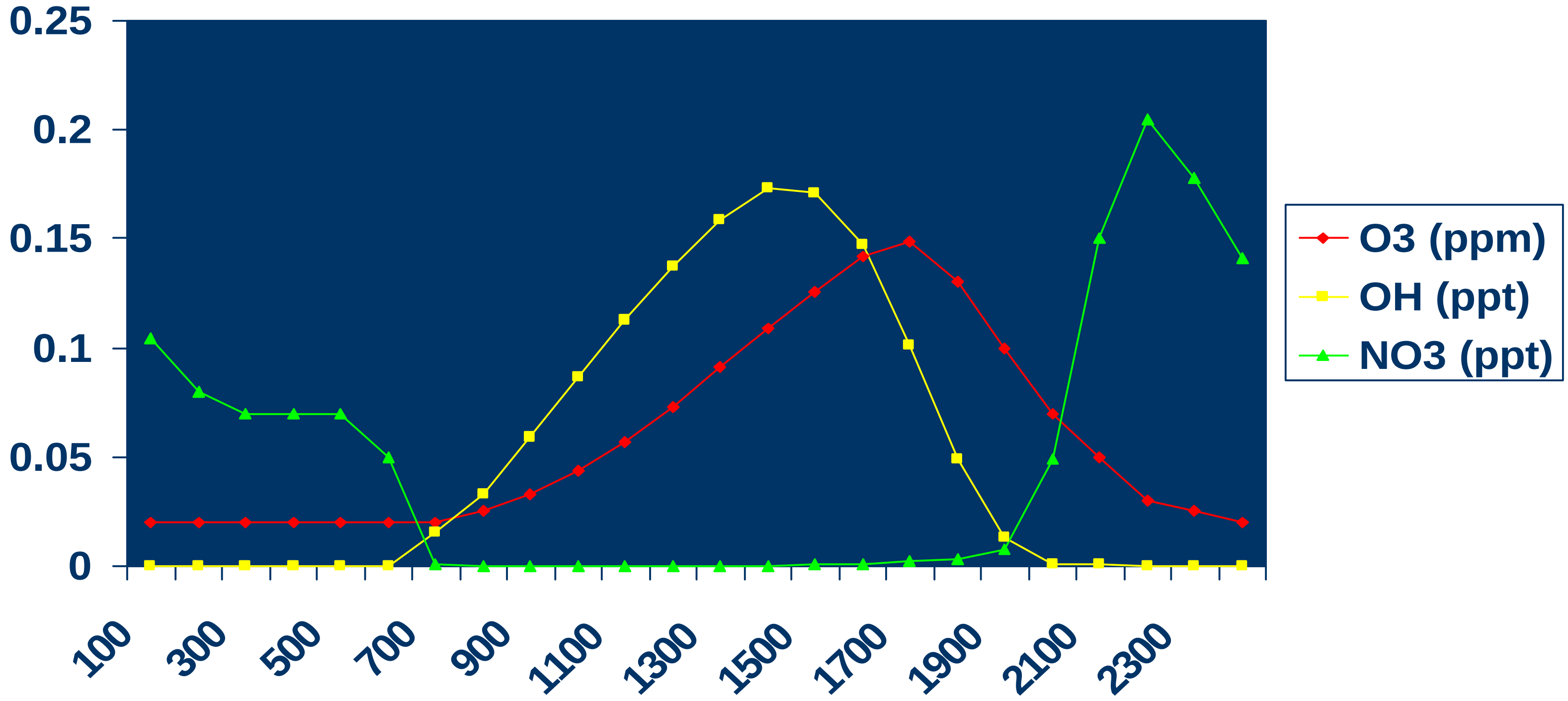
Chemical decay processes in the atmosphere (cont)

- Reaction with Ozone
  - With a few exceptions, only important for species with double bonds (1,3-butadiene, 1,3-dichloropropene) or particle-bound (POM)
  - Usually less important than OH reaction (but not always)
  - Ozone concentration varies throughout the day and throughout the year (20-80 ppb winter, 20-150 ppb summer)

Chemical decay processes in the atmosphere (cont)

- Reaction with NO3 radical
  - Only important at night, and only for a few species (POM, 1,3-butadiene)
  - Varies from about 0-1.0e10 in summer and 0.0-1.2e8 in winter

Typical diurnal variations in oxidants



Chemical decay processes in the atmosphere

- Photolysis in sunlight
  - Only important for species that absorb actinic radiation at wavelengths > 290 nm (formaldehyde, acetaldehyde, POM)
  - Can be extremely important during the day – but highly variable (HCHO photolysis rate 0.0-1.3e-4 in summer, 0.0-6.e-5 in winter)
- Other reactants in the gas phase
- Other reactants in aqueous and particle phases

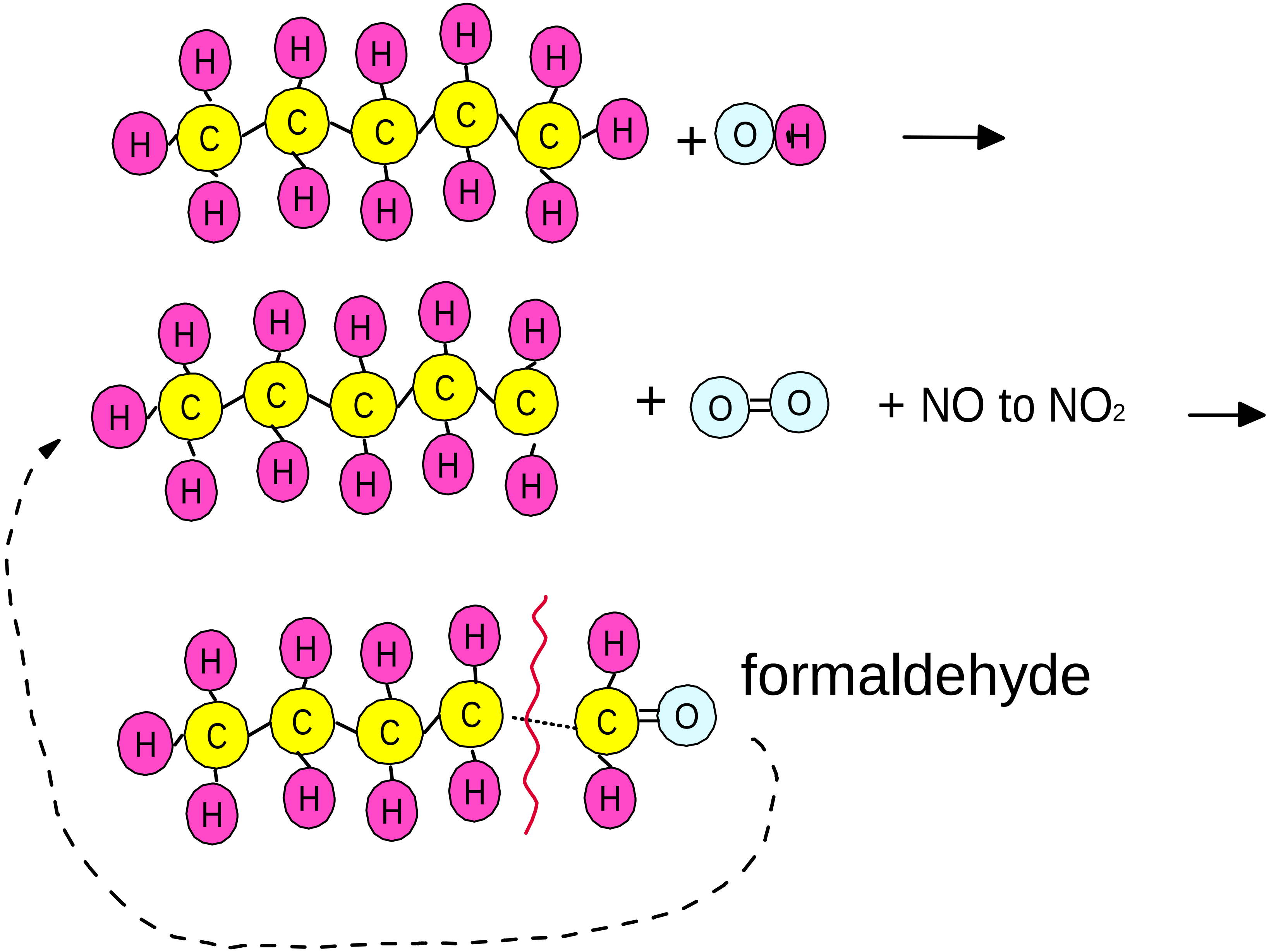
species	t1/2, summer	t1/2, winter	Time unit	Dominant reaction
formaldehyde	2	6	hours	photolysis
POM	2 to 7	23 to 117	hours	
1,3-butadiene	2	8	hours	OH, NO3
1,3-dichloropene	11 to 19	134 to 228	hours	OH
Chromium (VI)	16	16	hours	
Benzene	6	65	days	OH
Ethylene oxide	20	240	days	OH
Perchloroethylene	39	365	days	OH
Carbon tetrachloride	37	440	years	OH

Pollutant production processes in the atmosphere

- Air toxics can be produced from other air toxics as well as other VOCs
- Atmospheric formation is only important for certain species
- Can transform one state of a toxic to another
- Can be the major source of formaldehyde, acetaldehyde, and acrolein

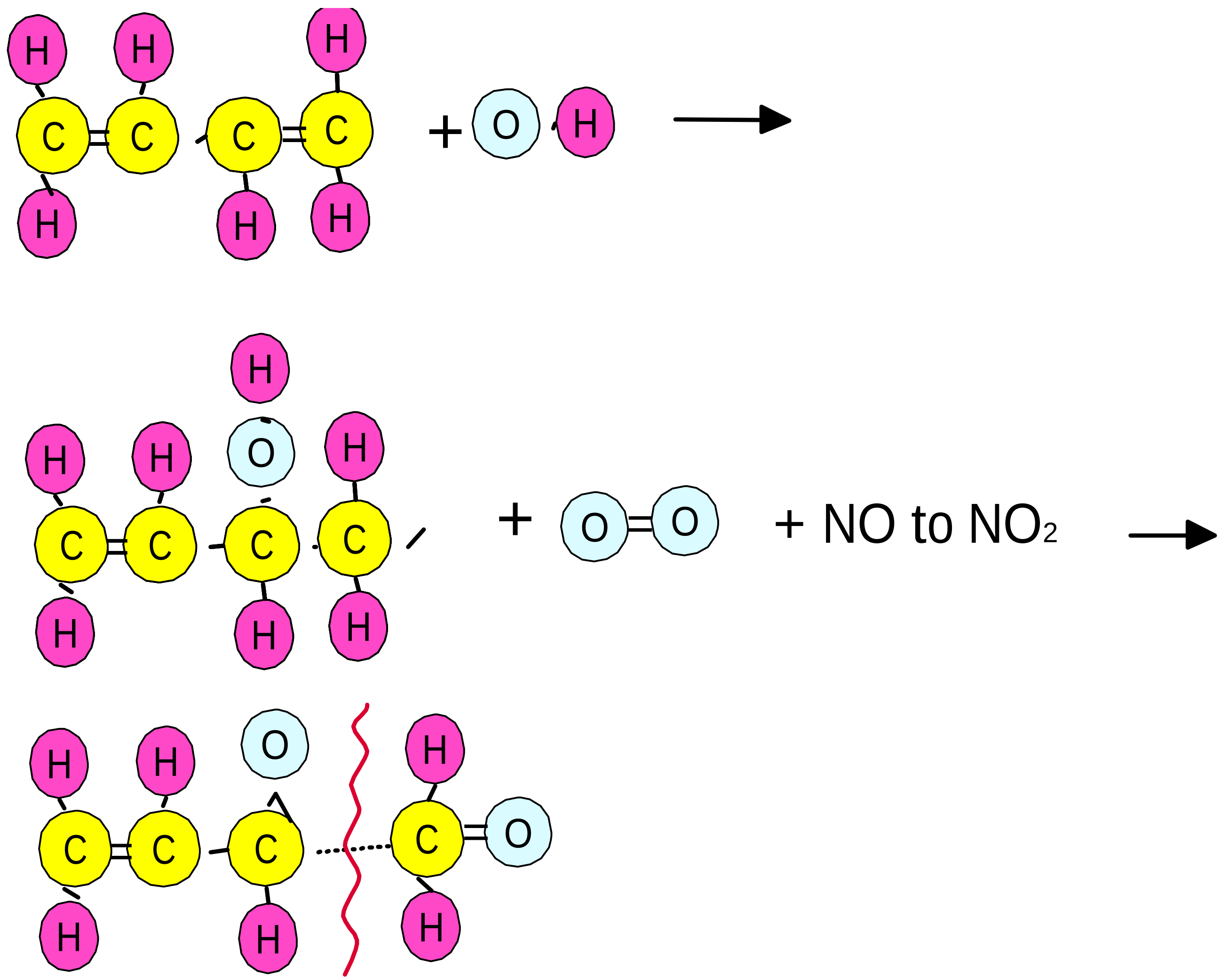
Pollutant production processes in the atmosphere (cont.)

- Formaldehyde and acetaldehyde
  - Can be formed from every VOC in the atmosphere
  - Major contributors are toluene, xylene, auto exhaust, biogenic hydrocarbons
  - Estimate 85-99% of these aldehydes are due to atmospheric formation, not emissions


+ NO to NO2
formaldehyde

Pollutant production processes in the atmosphere (cont.)

- Acrolein
  - Formed from the decay of 1,3-dienes (such as 1,3-butadiene) through cleavage of the double bond
- Other air toxics from Section 112 list of 189
  - 30 others with secondary sources
- Potential air toxics, including oxygenates and nitrated PAHs
- Semi-, alkaline, and transition metals
  - chromium, lead, arsenic, cadmium, beryllium, and mercury



acrolein formaldehyde

Implications for monitoring network design

- Some monitors should be placed downwind of major sources (not just air toxics sources)
- But not too far downwind
- Monitor major aldehyde precursors, even if they are not air toxics themselves
- Chemistry can be highly variable – both spatially and temporally

Implications for modeling studies

- Need to account for atmospheric chemistry if you are going to do a good job of predicting concentrations
- Atmospheric chemistry descriptions are not available or adequately verified for all pollutants
- There is really no good way to predict aldehyde concentrations with a dispersion model
- If you use a simpler model, must quantify the uncertainties

Relationship of air toxics chemistry to O3, PM2.5, and global warming

- One atmosphere
- Air toxic reaction products can form
  - Compounds that deposit to water or soil
  - Reactive species that increase formation of ozone and other oxidants
  - Semi-volatile species that form particulates
  - Greenhouse gases
- Controls in one are will impact other pollutants

Research needed to improve our understanding of air toxic chemistry

- Better understanding and descriptions of transition metal chemistry and products
- Better evaluation of model predictions of formaldehyde and acetaldehyde
- Improved understanding of potential toxicity of photochemically-produced compounds which are not on the list
- Improved ability to include complex chemistry in AQMs over long times and large domains